



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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| (51) International Patent Classification <sup>7</sup> :<br><br>C09J 4/00, G11B 17/24  |  | A1   | (11) International Publication Number: <b>WO 00/40663</b>    |
|   |  |  | (43) International Publication Date: 13 July 2000 (13.07.00) |
| <p>(21) International Application Number: PCT/IE00/00001</p> <p>(22) International Filing Date: 7 January 2000 (07.01.00)</p> <p>(30) Priority Data:<br/>60/115,402 8 January 1999 (08.01.99) US</p> <p>(71) Applicant (for all designated States except US): LOCTITE (R &amp; D) LIMITED [IE/IE]; Tallaght Business Park, Whitestown, Tallaght, Dublin 24 (IE).</p> <p>(72) Inventor; and</p> <p>(75) Inventor/Applicant (for US only): BIRKETT, David, P. [GB/IE]; 113 The Park, Sallins Road, Naas, County Kildare (IE).</p> <p>(74) Agents: LANE, Cathal, Michael et al.; Tomkins &amp; Co., 5 Dartmouth Road, Dublin 6 (IE).</p>   |  | <p>(81) Designated States: AE, AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), DM, EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SB), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published<br/>With international search report.</p> |  |
| <p>(54) Title: ADHESION PROMOTERS</p>   |  |  |  |
| <p>(57) Abstract</p> <p>The present invention relates to compositions useful as adhesion promoters for use in adhesive formulations to enhance the adhesion of cured adhesive formulations to surfaces on which the adhesive formulations are applied. More specifically, these adhesion promoter compositions are useful with or in (meth)acrylate-based adhesives, particularly in connection with (meth)acrylate-based adhesives that may be cured by exposure to radiation in the electromagnetic spectrum, and particularly for those destined for application in bonding polar plastics, such as polycarbonate or acrylic, notably in the manufacture of optical or video disk assemblies, medical devices such as needles, and electronic devices.</p> |  |  |  |

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ADHESION PROMOTERSBACKGROUND OF THE INVENTIONField of the Invention

5        The present invention relates to compositions useful as adhesion promoters for use in adhesive formulations to enhance the adhesion of cured adhesive formulations to surfaces on which the adhesive formulations are applied. More specifically, these adhesion promoter  
10      compositions are useful with or in (meth)acrylate-based adhesives, particularly in connection such adhesives that may be cured by exposure to radiation in the electromagnetic spectrum, and particularly for those destined for application in bonding polar plastics, such as polycarbonate  
15      or acrylic, notably in the manufacture of optical or video disk assemblies, medical devices (e.g., needles), and electronic devices.

Brief Description of Related Technology

20      Generally, surface preparation of many substrates prior to bonding is not only common, but often required to achieve strong adhesive bonds between the substrates.

25      Traditionally, in addition to mechanical surface treatments, such as roughening the substrate surface, chemical treatments have also been employed. Such chemical treatments are used to modify the physical structure of the surface, such as by etching, anodizing, cleaning or leaving an activator on, the surface, or may serve as one or more coatings to provide a mutually-compatible interface layer  
30      between the underlying substrate and the adhesive to be coated thereover. These pre-treatment coatings serve to promote the formation of physical and chemical intermolecular forces, thereby enhancing the strength of the adhesive bonds.

For instance, U.S. Patent No. 5,107,069 (Wichelhaus) discloses heat-activated adhesion promoters for treating surfaces prior to bonding. These promoters, useful with polymer fiber promoters, are applied directly to the 5 surface, and include a solvent mixture of a carbonyl compound (including unsaturated dicarboxylic acids and esters thereof, such as esters of maleic, crotonic and fumaric acids) with at least one unsaturated activated bond and a polymer containing a functional group (including 10 carboxylic, amine or hydroxy groups, such as polyesters, polyamides, polyethers, polyacrylates and polyurethanes).

European Patent Publication EP 601 725 discloses an adhesion promoter composition for improving adhesion of polyurethane-based adhesive compositions to substrate 15 surfaces. This adhesion promoter composition includes an ester, a polyisocyanate prepolymer which is compatible and functionally reactive with the polyurethane-based adhesive, and a solvent carrier unreactive with the prepolymer and ester.

U.S. Patent No. 5,314,562 (McDonnell) claims a 20 method of bonding a pair of substrates, at least one of which is a plastic substrate. The method includes the steps of applying to the substrate a primer solution of an adhesion-promoting ethylenediamine primer substance (in an 25 amount of between 0.01 and 0.75%), allowing the primer solution to dry, applying an  $\alpha$ -cyanoacrylate adhesive to one of the substrates, and joining the substrates.

In the context of cyanoacrylate adhesive bonding on non-polar substrates, such as a polyolefin, U.S. Patent 30 No. 4,869,772 (McDonnell) claims a method of bonding a non-polar substrate to another substrate using an adhesion-promoting primer comprising diazabicyclo or triazabicyclo compounds prior to applying an  $\alpha$ -cyanoacrylate adhesive.

In addition to surface pre-treating substrates with a primer chemical to promote adhesion prior to adhesive application, primer chemicals have been formulated directly into adhesive formulations to act as an adhesion promoter.

5 Such one-part adhesive systems are oftentimes more desirable to the end user because of convenience, ease of application and clean-up, and decreased process time.

Organosilicone compounds have been used to promote adhesion either applied as a primer or incorporated into adhesive formulations. Such compounds have been used to improve the strength and provide enhanced resistance to humid conditions. (See e.g., U.S. Patent No. 4,456,718.) Other well-known adhesion promoters include organotitanates, organic chromium and zirconium complexes.

15 In the context of anaerobic adhesives, U.S. Patent No. 5,811,473 (Ramm) claims a one-part primer activator composition including a non-combustible, non-ozone depleting liquid polyfluoroalkane having at least one carbon-hydrogen bond, an alkanol capable of forming an azeotropic mixture with the polyfluoroalkane, and a transition metal compound.

20 And in the specific use of adhesives for optical disk applications, U.S. Patent No. 5,698,285 (Kojima) speaks to a photocurable adhesive, which includes a radically polymerizable vinyl compound (including acryloyl morpholine), an acylphosphine oxide compound and an  $\alpha$ -aminobenzophenone compound as a photoinitiator. Other adhesives useful in connection with optical disks include those described in U.S. Patent Nos. 5,540,967 (Toide) and 5,663,211 (Kominami).

25 In connection with coating compositions, such as photocurable paints and lacquers, U.S. Patent No. 4,348,427 (Priola) claims a method of covering surfaces consisting of applying to the surface a composition of epoxy-acrylic resins, urethane-acrylate resins and monovinylic compounds

of the formula,  $\text{CH}_2=\text{CH}-\text{NR}-\text{X}-\text{R}'$ , and irradiating the composition. Examples of these monovinylic compounds are given at col. 2, lines 31-39 as N-vinylmethylbutyramide, N-vinylmethylbenzamide, N-vinylmethylacetamide, N-vinylpropylacetamide, N-vinylphenylacetamide, N-vinylcaprolactam, N-vinyl-2-piperidone, N-vinylmethyl-N<sup>1</sup>-dimethylurea, N-vinylbutyl-p-tolucacaulphonamide, N-vinyl-N-methyl-p-toluenesulphonamide, N-vinylmethyl-N<sup>1</sup>-dimethyl-N<sup>3</sup>-dimethylphosphoramide, and N-vinylmethylisobutyramide.

10 And U.S. Patent No. 3,252,819 (Cobb) speaks to the use of N-vinyl amides as plasticizers for blending with polyurethanes as potting compounds, examples of which are given at col. 3, line 35 - col. 4, line 41.

15 Heretofore, N-vinyl pyrrolidone ("NVP") had been used to improve adhesion of adhesive compositions to plastic substrates. While NVP worked well for its intended purpose, it was discovered to be a suspected carcinogen. Accordingly, the desirability of using NVP waned in favor of more "user-friendly" alternatives.

20 Since then, N,N'-dimethylacrylamide has been used in or with adhesive formulations to promote adhesion on the substrate on which the adhesive is applied, including optical disk substrates. Recently, however, N,N'-dimethylacrylamide has come under scrutiny in certain 25 industrialized countries due to reports claiming exposure thereto may have harmful health consequences. These reports have led to the promulgation of severe label warning requirements. Such severe label warnings is perceived as undesirable in the marketplace, because many end users do 30 not desire to have their workers exposed to such materials during manufacture.

As a result, finding replacement materials for N,N'-dimethylacrylamide as an adhesion promoter has become an important issue to adhesive formulators in order to

comply with regulatory mandates while still providing a commercially desirable adhesive formulation. Acryloyl morpholine is one suitable replacement, but others would be desirable particularly in view of supply shortages or other 5 events impacting on the availability of that material.

There is therefore a need for an adhesion promoter composition that improves adhesion of an adhesive formulation with, or in, which it is to be used, that includes N,N'-dimethylacrylamide at levels no greater than 10 3% by weight of the composition or the adhesive formulation in which it is used (whichever is greater), or preferably for some end users not at all.

#### SUMMARY OF THE INVENTION

15 The present invention relates to compositions useful as adhesion promoters for use in adhesive formulations to enhance the adhesion of cured adhesive formulations to surfaces on which the adhesive formulations are applied.

20 More specifically, these compositions are useful with or in (meth)acrylate-based adhesive formulations, particularly for those destined for application in bonding polar plastics, such as polycarbonate or acrylic, notably in the manufacture of optical or video disk assemblies. The 25 adhesive formulations may also be advantageously employed in the manufacture of medical devices, such as needles, and electronic devices.

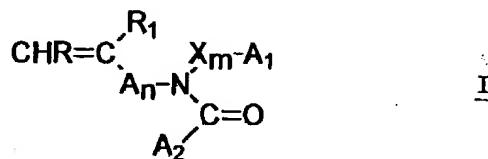
Desirably, these formulations are curable through exposure to radiation in the electromagnetic spectrum.

30 The adhesion promoter compositions of this invention include N,N'-dimethylacrylamide at levels not greater than 3% by weight of the composition or the adhesive formulation in which it is used (whichever is greater). At such levels, present regulations do not require or suggest

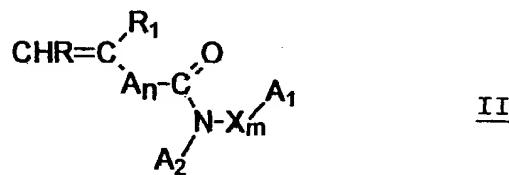
severe warnings on container labels. Preferably, however, the inventive adhesion promoter compositions do not include N,N'-dimethylacrylamide.

5 The inventive adhesion promoter compositions include an adhesion promoter for improving adhesion of adhesive compositions to substrate surfaces, comprising one or more compounds within the following structures I and II:

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where R and R<sub>1</sub> may be the same or different and may be selected from hydrogen or C<sub>1-3</sub> alkyl, or either of which may join to form a cyclic ring structure of between 4 and 10 ring atoms with themselves, or with A<sub>1</sub> or A<sub>2</sub> as defined below;

20 X and A may be the same or different and may be selected from -(CR<sub>2</sub>R<sub>3</sub>)<sub>p</sub>-, where R<sub>2</sub> and R<sub>3</sub> may be the same or different and may be selected from

25 hydrogen or C<sub>1-3</sub> alkyl, and p is an integer of from 0 to 3,

30 an alklyene group (-CR<sub>4</sub>=CR<sub>5</sub>-, where R<sub>4</sub> and R<sub>5</sub> may be the same or different and may be selected from hydrogen or C<sub>1-3</sub> alkyl),

an arylene group (such as p-phenylene, -C<sub>6</sub>H<sub>4</sub>-),  
a carbonyl group, -CO-,

heteroatoms [such as -O-, -S-, -NR<sub>4</sub>- (where R<sub>4</sub> may be selected from hydrogen or C<sub>1-3</sub> alkyl)], and combinations thereof;

m and n may be the same or different and are 0 or 1;

5 and

A<sub>1</sub> and A<sub>2</sub> may be the same or different and may be selected from hydrogen, C<sub>1-3</sub> alkyl, alkenyl (such as vinyl and allyl), aryl, aryl heterocyclic, acidic groups (such as -CO<sub>2</sub>H, -SO<sub>3</sub>H, and -PO(OH)<sub>2</sub> or salts or esters thereof), and basic groups (such as -NR<sub>4</sub>R<sub>5</sub>, where R<sub>4</sub> and R<sub>5</sub> are as defined above, or salts thereof, such as onium salts).

10 While the adhesion promoters of the present invention are especially designed for use in (meth)acrylate-based adhesives, they may be useful in other types of adhesives, as well as in a surface primary application on substrates, where the promoter is applied or coated on the surface of the substrate in one part as a primer coat and the adhesive as a second part is thereafter applied or coated onto the promoter coat, which is now present on the substrate surface.

15 Of course, adhesive formulations of which these adhesion promoter compositions are present as a constituent are also included within the scope of the invention.

20 In addition, reaction products of such adhesive formulations are also included within the scope of the invention.

25 The present invention also provides methods of preparing and using the inventive adhesion promoter composition and inventive adhesive formulation.

30 This invention will be more readily understood by a reading of the "Detailed Description of the Invention", together with the figures.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1 shows cross-section depictions of optical disks -- single sided (A), double sided, single layer(B) and single sided, dual layer (C) -- assembled with an adhesion promoter in an adhesive formulation in accordance with the present invention.

FIG. 2 shows a cross-section of an optical disk assembled with an adhesion promoter in an adhesive formulation in accordance with the present invention.

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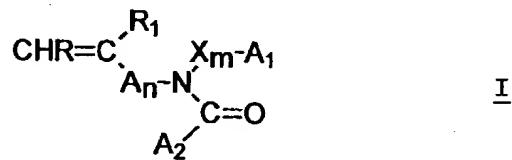
DETAILED DESCRIPTION OF THE INVENTION

The adhesion promoter compositions of the present invention are advantageously used in or with (meth)acrylate-based adhesive compositions.

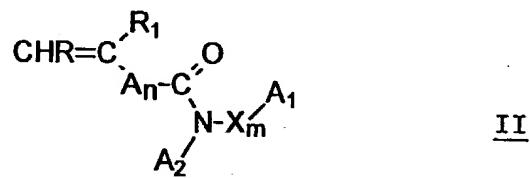
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These adhesion promoter compositions improve adhesion of cured adhesive formulations to substrate surfaces. The adhesion promoter includes one or more compounds within the following structures I and II:

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where R and R<sub>1</sub> may be the same or different and may be selected from hydrogen or C<sub>1-3</sub> alkyl, or either of which may join to form a cyclic ring structure of between 4 and 10 ring atoms with themselves, or with A<sub>1</sub> or A<sub>2</sub> as defined below;

X and A may be the same or different and may be selected from  $-(CR_2R_3)_p-$ , where R<sub>2</sub> and R<sub>3</sub> may be the same or different and may be selected from

hydrogen or  $C_{1-3}$  alkyl, and p is an integer of from 5 to 3,

an alklyene group ( $-\text{CR}_4=\text{CR}_5-$ , where  $\text{R}_4$  and  $\text{R}_5$  may be the same or different and may be selected from hydrogen or  $\text{C}_{1-3}$  alkyl),

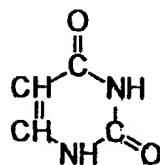
10 a carbonyl group,  $\text{-CO-}$ ,  
heteroatoms [such as  $\text{-O-}$ ,  $\text{-S-}$ ,  $\text{-NR}_4^-$  (where  $\text{R}_4$  may  
be selected from hydrogen or  $\text{C}_{1-3}$  alkyl)], and combinations  
thereof;

m and n may be the same or different and are 0 or 1;

A<sub>1</sub> and A<sub>2</sub> may be the same or different and may be selected from hydrogen, C<sub>1-3</sub> alkyl, alkenyl (such as vinyl and allyl), aryl, aryl heterocyclic, acidic groups (such as -CO<sub>2</sub>H, -SO<sub>3</sub>H, and -PO(OH)<sub>2</sub> or salts or esters thereof), and basic groups (such as -NR<sub>4</sub>R<sub>5</sub>, where R<sub>4</sub> and R<sub>5</sub> are as defined above, or salts thereof, such as onium salts).

Among those compounds within the structure I particularly useful as adhesion promoters in the present invention are N-methyl-N-vinyl acetamide (where R and R<sub>1</sub> are hydrogen, n and m are 0, and A<sub>1</sub> and A<sub>2</sub> are CH<sub>3</sub>); N-vinylcaprolactam (where R and R<sub>1</sub> are hydrogen, m and n are 0, and A<sub>1</sub> and A<sub>2</sub> join to form a -(CH<sub>2</sub>)<sub>5</sub>- group which together with the -N-CO- group forms a seven membered ring); N-vinylphthalimide (where R and R<sub>1</sub> are hydrogen, n is 0, X is carbonyl (-CO-), m is 1, and A<sub>1</sub> and A<sub>2</sub> join to form an o-phenylene (-C<sub>6</sub>H<sub>4</sub>-) group); Uracil (where R<sub>1</sub> is hydrogen, A is carbonyl (-CO-), n is 1, A<sub>2</sub> is -NH- and R and A<sub>2</sub> taken together join to form a six membered ring structure) as follows in structure III:

- 10 -

III

5 and N-vinylpyrrolidone (where R and R<sub>1</sub> are hydrogen, m and n are 0, and A<sub>1</sub> and A<sub>2</sub> join to form a -(CH<sub>2</sub>)<sub>3</sub>- group which together with the -N-CO- group forms a five membered ring structure.

10 Among the compounds within the structure II particularly useful as adhesion promoters in the present invention are diacetone acrylamide (where R, R<sub>1</sub> and A<sub>2</sub> are hydrogen, n is 0, X is -C(CH<sub>3</sub>)<sub>2</sub>-CO-, m is 1 and A<sub>1</sub> is CH<sub>3</sub>); 2-acrylamido 2-methyl 1-propane sulphonic acid (where R, R<sub>1</sub> and A<sub>2</sub> are hydrogen, n is 0, X is -C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-, m is 1, and A<sub>1</sub> is CH<sub>3</sub>); and 2-methacryloxyethyl phenyl urethane (where R and A<sub>2</sub> are hydrogen, A is -C(=O)CH<sub>2</sub>CH<sub>2</sub>O-, n is 1 m is 0 and A<sub>1</sub> is phenyl).

15 In addition, N,N'-dimethylacrylamide (where R and R<sub>1</sub> are hydrogen, n and m are 0, and A<sub>1</sub> and A<sub>2</sub> are CH<sub>3</sub>) may be used in combination with one or more of the previously noted compounds in the adhesion promoter compositions.

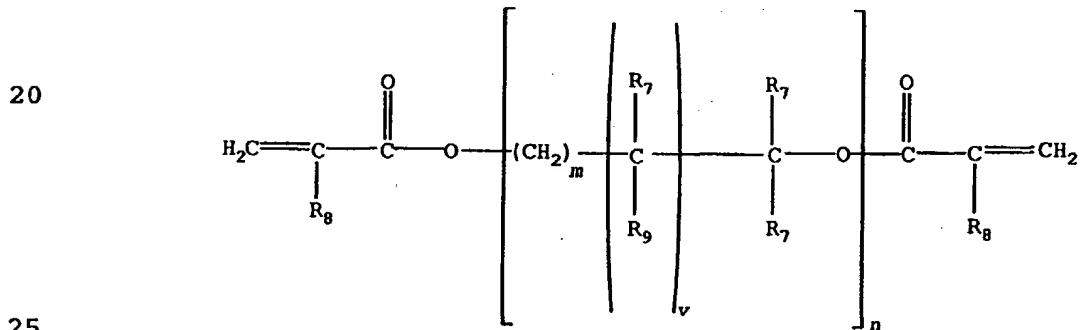
20 Moreover, acryloyl morpholine (where R and R<sub>1</sub> are hydrogen, n is 0, X is -CH<sub>2</sub>CH<sub>2</sub>O-, m is 1, and A<sub>1</sub> and A<sub>2</sub> join to form a -(CH<sub>2</sub>)<sub>2</sub>- group which together with X and the N atom form a six membered ring structure) may be used in combination with one or more of the previously noted compounds in the adhesion promoter compositions.

25 When used in the adhesive formulation, the adhesion promoter composition should be used in an amount from about 2% to about 30% by weight of the composition, such as about 5% to about 20% by weight, and particularly about 15% by weight.

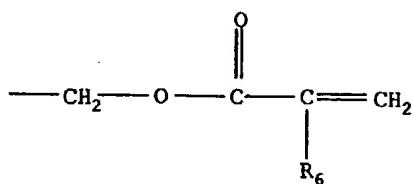
30 The (meth)acrylates that may be used in the adhesive composition in accordance with this invention

5 include a wide variety of materials represented by  $H_2C=CGCO_2R_6$ , where G may be hydrogen, halogen or alkyl of 1 to about 4 carbon atoms, and  $R_6$  may be selected from alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, aralkyl or aryl groups of 1 to about 16 carbon atoms, any of which may be optionally substituted or interrupted as the case may be with silane, silicon, oxygen, halogen, carbonyl, hydroxyl, ester, carboxylic acid, urea, urethane, carbamate, amine, amide, sulfur, sulonate, sulfone and the like.

10 More specific acrylate monomers particularly desirable for use herein include polyethylene glycol di(meth)acrylates, bisphenol-A di(meth)acrylates, such as ethoxylated bisphenol-A (meth)acrylate ("EBIPMA") and tetrahydrofuran (meth)acrylates and di(meth)acrylates, 15 hydroxypropyl (meth)acrylate, hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate, an acrylate ester corresponding to the structure shown below:



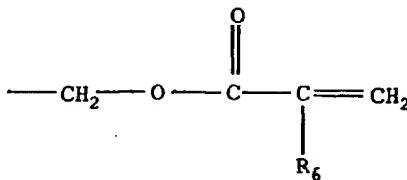
where  $R_7$  may be selected from hydrogen, alkyl of 1 to about 4 carbon atoms, hydroxyalkyl of 1 to about 4 carbon atoms or



R<sub>8</sub> may be selected from hydrogen, halogen, and alkyl of 1 to about 4 carbon atoms;

R<sub>9</sub> may be selected from hydrogen, hydroxy and

5



10 m is an integer equal to at least 1, e.g., from 1 to about 8 or higher, for instance, from 1 to about 4;

n is an integer equal to at least 1, e.g., 1 to about 20 or more; and

v is 0 or 1.

15 Of course, combinations of these (meth)acrylate monomers may also be used.

Particularly desirable (meth)acrylates for use herein include urethane (meth)acrylates (such as those available commercially in the "PHOTOMER" 6000 series from Henkel KGAA, Dusseldorf, Germany or the "EBECRYL" series 20 from UCB Radcure Inc., Smyrna, Georgia), ethoxylated phenol monoacrylate epoxy acrylates ["(EO)PEA"], such as "PHOTOMER" 4039 available commercially from Henkel, ethoxylated trimethylol propane triacrylate ["(EO)TMPTA"], such as "SARTOMER" SR 454 available commercially from Sartomer Co., 25 Exton, Pennsylvania, and epoxy acrylates (such as those available commercially in the "PHOTOMER" 3000 series from Henkel KGAA or the "EBECRYL" series from UCB, such as "EBECRYL" 3500). Of course, combinations of these (meth)acrylates may be used as well.

30 In the aspect of the invention where the adhesive formulations are curable through exposure to radiation in the electromagnetic spectrum, a photoinitiator component should also be included. The photoinitiators that may be used in the adhesive compositions of the present invention

include, but are not limited to, photoinitiators available commercially from Ciba-Geigy Corp., Tarrytown, New York under the "IRGACURE" and "DAROCUR" tradenames, specifically "IRGACURE" 184 (1-hydroxycyclohexyl phenyl ketone), 907 (2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one), 5 369 (2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone), 500 (the combination of 1-hydroxy cyclohexyl phenyl ketone and benzophenone), 651 (2,2-dimethoxy-2-phenyl acetophenone), 1700 (the combination of bis(2,6-dimethoxybenzoyl-2,4-,4-trimethyl pentyl phosphine oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one) and "DAROCUR" 1173 (2-hydroxy-2-methyl-1-phenyl-1-propane) and 4265 (the combination of 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide and 2-hydroxy 2-methyl-1-phenyl-propan-1-one); photoinitiators available 10 commercially from Union Carbide Chemicals and Plastics Co. Inc., Danbury, Connecticut under the "CYRACURE" tradename, such as "CYRACURE" UVI-6974 (mixed triaryl sulfonium hexafluoroantimonate salts) and UVI-6990 (mixed triaryl sulfonium hexafluorophosphate salts); and the visible light 15 [blue] photoinitiators, dl-camphorquinone and "IRGACURE" 784DC. Of course, combinations of these materials may also 20 be employed herein.

Photoinitiators particularly suitable for use 25 herein include ultraviolet photoinitiators, such as 2,2-dimethoxy-2-phenyl acetophenone (e.g., "IRGACURE" 651), and 2-hydroxy-2-methyl-1-phenyl-1-propane (e.g., "DAROCUR" 1173) and the ultraviolet/visible photoinitiator combination of bis(2,6-dimethoxybenzoyl-2,4-,4-trimethylpentyl) phosphine 30 oxide and 2-hydroxy-2-methyl-1-phenyl-propan-1-one (e.g., "IRGACURE" 1700), as well as the visible photoinitiator bis( $\eta^5$ -2,4-cyclopentadien-1-yl)-bis[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]titanium (e.g., "IRGACURE" 784DC).

When used, the photoinitiator may be used in an amount of from about 0.5 to about 10% by weight of the composition, such as about 2 to about 7% by weight.

Alternatively, the adhesive formulations of the present invention may be rendered curable anaerobically, when an anaerobic cure-inducing composition is included in the formulation, and the formulation is applied to a substrate that is then placed in an environment in which air is excluded.

Such an anaerobic cure-inducing composition useful in the present invention includes a variety of components, such as amines (including amine oxides, sulfonamides and triazines). A desirable composition to induce cure in accordance with the present invention includes saccharin, toluidenes, such as N,N-diethyl-p-toluidene and N,N-dimethyl-o-toluidene, acetyl phenylhydrazine, and maleic acid. Of course, other materials known to induce anaerobic cure may also be included or substituted therefor. See e.g., Loctite U.S. Patent Nos. 3,218,305 (Krieble), 4,180,640 (Melody), 4,287,330 (Rich) and 4,321,349 (Rich). Quinones, such as napthoquinone and anthraquinone, may also be included to scavenge free radicals which form.

The adhesion promoter compositions and adhesive formulations of the present invention may be used on a variety of different surfaces, including metallic surfaces, such as steel, aluminum, copper and zinc bichromate. In addition, the present invention may be used on ordinarily difficult to bond to substrates, such as non-ferrous materials, plastic and wood.

The present invention also provides methods of using the adhesion promoter composition to enhance adhesion of (meth)acrylate-based adhesive compositions to a substrate surface. In one aspect of the inventive methods, the method includes the steps of applying the adhesion promoter to a

substrate surface and thereafter applying the adhesive formulation over the adhesion promoter-coat substrate.

In another aspect of the inventive methods, the method includes the step of admixing the adhesion promoter composition into the adhesive formulation, and thereafter applying the adhesive formulation onto the substrate.

5 The present invention also provides a method of preparing the adhesive formulation, a step of which includes admixing the adhesion promoter composition into the adhesive 10 formulation.

This invention provides methods of curing the adhesive formulation. In addition, the present invention further provides articles manufactured with the inventive adhesion promoter compositions and adhesive formulations. 15 The commonality of these articles resides in that each has at least one surface having applied thereto the inventive adhesion promoter composition, adhesive formulations or both.

20 Now, with reference to FIG. 1, the present invention will be described in the context of manufacturing an optical disk assembly.

25 FIG. 1 shows a cross-section of optical disk assemblies labeled A, B and C, each of which is designated as 10. With the assemblies is also shown the focal point of a lens 11 for reading information prerecorded on the disks.

These assemblies of various configurations of pre-recorded high density optical disks. Typically, data is stamped into a circular transparent substrate 1, such as one constructed from polycarbonate. A reflective layer 2, 30 typically aluminum, is then deposited over the data-stamped substrate. This aluminum-deposited data-stamped substrate 1/2 may then be bonded with a bonding adhesive 3 to a second substrate 4, which may also be constructed from polycarbonate, but having no data stamped therein. This

assembly is representative of a single sided disk assembly (A).

5 In an alternative embodiment, the aluminum-deposited data-stamped substrate 1/2 may be bonded with a bonding adhesive 3 to another aluminum-deposited data-stamped substrate 1/2. This assembly is representative of a double sided, single layer disk assembly (B).

10 In another alternative embodiment, the aluminum-deposited data-stamped substrate 1/2 may be bonded with a bonding adhesive 3 to a data-stamped substrate 4 coated with a layer that is both semi-transparent and semi-reflective 5. This assembly is representative of a single sided, dual layer disk assembly (C).

15 Two methods are commonly used to form the adhesive layer. In the first method, adhesive may be dispensed close to the center of one of the substrates, then spread over the entire surface of the substrate using centripetal force, as the substrate spins about a central post. The second substrate is then mated with the adhesive-coated substrate, 20 and held in place for the requisite period of time (and in the case of photocurable adhesives, exposed to radiation in the appropriate range of the electromagnetic spectrum) to cure the adhesive and form the assembly.

25 In the second method, the two substrates may be brought together, and the adhesive injected between them at a location close to the center. The adhesive can then be spread out over the entirety of the internal surfaces of the assembly using the weight of the upper substrate to force the adhesive outward, capillary action, centripetally as 30 above, or a combination thereof. In the case of photocurable adhesives, the assembly is exposed to radiation in the appropriate range of the electromagnetic spectrum to cure the adhesive and form the assembly.

As regards recordable disks, reference to FIG. 2 is illustrative in which, a recording layer 22 is formed on a transparent substrate 21 of resin, such as, for example, polycarbonate, and a protective film 23 is formed over the recording layer 22. The substrate 21, the layer 22 and the film 23 form a disk unit 24. Two such disk units 24, are bonded to each other at the exposed surfaces of the respective protective films 23 with an adhesive layer 25 to form the optical disk 20. In bonding the disk units 24 together, the inventive adhesion promoter composition may initially be coated on either or both of such exposed surfaces, and thereafter an adhesive formulation may be applied over the adhesion promoter-coated surface. Alternatively, the inventive adhesive formulation may be coated on either or both of such exposed surfaces.

In another technique for bonding two disk units 24, a first disk unit 24 is positioned with the recording layer 22 facing upward. The inventive adhesive formulation is applied over the protective film 23 on the recording layer 22 in generally concentric circles. A second disk unit 24 is aligned with the first disk unit 24 by a center shaft of the disk manufacturing apparatus, and the protective film 23 of the second disk unit 24 is brought into contact with the coating of adhesive formulation. The adhesive is allowed to spread over the entire surfaces of the protective films of the resultant assembly due to the weight of the disk unit and by virtue of capillary action, and the adhesive is caused to cure to bond the two disk units together.

In the case of adhesive formulations curable by exposure to electromagnetic radiation, the adhesive layer is exposed to such light from the back side of the bonding surface(s).

If the film thickness of the protective film for the recording layer of the optical disk becomes undesirably thick, in certain instances, one or more of the substrates used to assemble the disk unit may tend to warp. A 5 reproducing apparatus may misread or be prevented from reading the recorded information on a warped disk. Therefore, it is important to ensure that the disk thickness of the protective film does not exceed the thickness recited above. The adhesive formulations to be used in a spin 10 coating method, as described above, should have a low viscosity, such as less than about 900 mPa.s, and desirably below about 400 mPa.s, such as below about 250 mPa.s for coating through capillary action.

15

#### EXAMPLES

Adhesive formulations curable upon exposure to ultraviolet radiation were prepared with the following components as set forth in Table 1.

20

Table 1

| Component         | wt%               |
|-------------------|-------------------|
| (Meth)acrylate    | Urethane Acrylate |
|                   | Epoxy Acrylate    |
|                   | (EO) TMPTA        |
|                   | (EO) PEA          |
| Photoinitiators   | IRGACURE 184      |
|                   | TPO               |
| Adhesion Promoter | See below         |

The adhesion promoters included N-vinyl caprolactam (Sample No. 1), N-methyl-N-vinyl acetamide (Sample No. 2) and N-vinyl phthalimide (Sample No. 3).

The formulations were prepared by mixing together the individual (meth)acrylate constituents, the photoinitiators and the adhesion promoter in any order.

5 The samples were each applied onto the surface of circular substrates made from polycarbonate or polymethyl methacrylate. In the manufacture of optical disks, the circular substrates are of the same dimension and aligned concentrically. The adhesive formulation is introduced between the substrates at a point toward their centers.

10 Upon spinning the substrates about a rotating centerpost, the adhesive formulation spins away from the center to coat substantially the entirety of the facing substrate surfaces. The optical disk assembly is then exposed to radiation in the electromagnetic spectrum, particularly ultraviolet

15 radiation, to cure the adhesive formulation.

In Table 2 below, a variety of additives, included in the adhesion promoter composition and/or adhesive formulation for the intended purpose of promoting adhesion to the substrates, are set forth to which reference was made 20 in Table 1. Also, the viscosity, tack free time, fixture time, and bond strength to polycarbonate ("PC") and polymethyl methacrylate ("PMMA") substrates for these additives are set forth in Table 2.

Table 2

| Sample | Additive                                       | Viscosity<br>(cps) | Tack<br>Free<br>time<br>(sec) | Fixture<br>Time<br>(sec) | Bond Strength<br>(3 sec $\times$ 50<br>mW/cm $^2$ ) (N/mm $^2$ ) |      |
|--------|--|--------------------|-------------------------------|--------------------------|--|------|
|        |  |                    |                               |                          | PC   | PMMA |
| A      | N-Vinylphthalimide                             | 946.5              | <1.5                          | 2<3                      | 1.12   | 1.7  |
| B      | N-Vinylcaprolactam                             | 430.3              | <1.5                          | <1                       | 2.12   | 1.3  |
| C      | N-Methyl-N'-vinylacetamide                     | 219.2              | <1.5                          | <1                       | 2.6  | 1.4  |
| D      | 2-Acrylamido-2-methyl-1-propane sulphonic acid | 3600               | <1.5                          | 1<2                      | 1.08   | 1.0  |
| E      | Urethane                                       | 489                | <1.5                          | 2<3                      | 0.2  | 0.2  |
| F      | Diacetone Acrylamide                           | 1211               | <1.5                          | <1                       | 1.52   | 1.3  |
| G      | Acryloyl Morpholine                            | 658.7              | <1.5                          | <1                       | 1.44   | 1.6  |
| H      | 1-Vinyl-2-Pyrrolidone                          | 276.1              | <1.5                          | <1                       | 2.9  | 1.6  |
| I      | N,N'-Dimethyl Acrylamide                       | 213.9              | <1.5                          | <1                       | 1.58   | 1.3  |
| J      | 2-Methacryloxy ethyl Phenylurethane            | 1641               | <1.5                          | 2<3                      | 1.1  | 0.9  |
| K      | (EO) PEA (Control)                             | 625.8              | <1.5                          | <1                       | 0.7  | 0.6  |
| L      | Uracil   | 4420               | <1.5                          | 1<2                      | 1.12   | 0.9  |

As can be seen from the data shown in Table 2, Samples A-D, F, H, J and L show improved adhesion in terms of bond strength to the PC and PMMA substrates over the control sample (Sample K) in which no adhesion promoter within the scope of this invention is included or urethane (Sample E) which individually falls outside the scope of the invention as it contains no vinylic group to become incorporated into the polymeric matrix of the cured adhesive formulation. The known adhesion promoters, acryloyl morpholine (Sample G) and N,N'-dimethylacrylamide (Sample I), despite other shortcomings, are shown to have excellent bond strength. Of course, these materials, while individually outside the scope of the present invention, may be used in combination with the adhesion promoters represented within structures I and II to confer improved properties to adhesion promoter compositions and/or adhesive

- 21 -

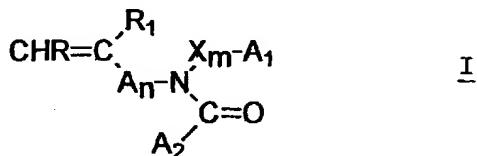
formulations with which the adhesion promoter combination is used.

The full scope of the present invention will be measured by the claims.

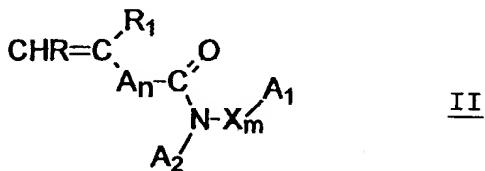
What is Claimed is:

1. An adhesion promoter composition for improving the adhesion of adhesive formulations to substrate surfaces, comprising at least one compound within the following structures:

5



10



15

wherein R and R<sub>1</sub> may be the same or different and may be selected from the group consisting of hydrogen and C<sub>1-3</sub> alkyl, or either of which may join to form a cyclic ring structure of between 4 and 10 ring atoms with themselves, or with A<sub>1</sub> or A<sub>2</sub> as defined below;

20

X and A may be the same or different and may be selected from the group consisting of:

-(CR<sub>2</sub>R<sub>3</sub>)<sub>p</sub>-, wherein R<sub>2</sub> and R<sub>3</sub> may be the same or different and may be selected from the group consisting of hydrogen and C<sub>1-3</sub> alkyl and p is an integer of from 0 to 3,

an alkylene group,  
an arylene group,  
a carbonyl group,  
heteroatoms, and combinations thereof;

30

m and n may be the same or different and are selected from 0 or 1; and

A<sub>1</sub> and A<sub>2</sub> may be the same or different and may be selected from the group consisting of hydrogen, C<sub>1-3</sub> alkyl,

35

alkenyl, aryl, aryl heterocyclic, acidic groups, and basic groups;

provided that when these structures embrace acryloyl morpholine and/or N,N'-dimethylacrylamide, the composition includes at least one other compound within the structures I and/or II.

2. The composition according to Claim 1, wherein the compound is N-methyl-N'-vinyl acetamide.

3. The composition according to Claim 1, wherein the compound is N-vinyl caprolactam.

4. The composition according to Claim 1, wherein the compound is N-vinyl phthalimide.

5. The composition according to Claim 1, wherein the compound is Uracil.

6. The composition according to Claim 1, wherein the compound is diacetone acrylamide.

7. The composition according to Claim 1, wherein the compound is 2-acrylamido, 2-methyl propane sulfonic acid.

8. The composition according to Claim 1, wherein the compound is 2-methacryloxyethyl phenyl urethane.

9. The composition according to Claim 1, wherein the adhesive formulation comprises a (meth)acrylate compound.

10. An adhesive formulation comprising:

- (a) a (meth)acrylate component; and
- (b) an adhesion promoter composition

according to Claim 1.

11. The formulation according to Claim 10,  
wherein the (meth)acrylate component comprises a member within  
the structure,  $H_2C=CGCO_2R_6$ , wherein G may be hydrogen, halogen  
or alkyl of 1 to about 4 carbon atoms, and  $R_6$  may be selected  
5 from alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl,  
aralkyl or aryl groups of 1 to about 16 carbon atoms, any of  
which may be optionally substituted or interrupted as the case  
may be with silane, silicon, oxygen, halogen, carbonyl,  
hydroxyl, ester, carboxylic acid, urea, urethane, carbamate,  
10 amine, amide, sulfur, sulonate, and sulfone.

12. The formulation according to Claim 10,  
wherein the adhesion promoter composition is present in an  
amount within the range of from about 2% to about 30% by  
weight of the formulation.

13. The formulation according to Claim 10,  
wherein the adhesion promoter composition is present in an  
amount within the range of from about 5% to about 20% by  
weight of the formulation.

14. The formulation according to Claim 10,  
wherein the adhesion promoter composition is present in an  
amount of about 15% by weight of the formulation.

15. The formulation according to Claim 10,  
further comprising a photoinitiator component.

16. The formulation according to Claim 15, wherein the photoinitiator component is a member selected from the group consisting of 1-hydroxycyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino propan-1-one, benzophenone, 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone, 2,2-dimethoxy-2-phenyl acetophenone, bis(2,6-dimethoxybenzoyl-2,4-,4-trimethylpentyl) phosphine oxide, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-2-methyl-1-phenyl-1-propane, 2,4,6-trimethylbenzoyldiphenyl-phosphine oxide, 2-hydroxy 2-methyl-1-phenyl-propan-1-one, mixed triaryl sulfonium hexafluoroantimonate salts, mixed triaryl sulfonium hexafluorophosphate salts, visible light [blue] photoinitiators, dl-camphorquinone, and combinations thereof.

17. The formulation according to Claim 10, further comprising an anaerobic cure-inducing composition.

18. An article of manufacture assembled using the adhesion promoter composition according to Claim 1.

19. An article of manufacture assembled using the adhesive formulation according to Claim 10.

20. A method of using an adhesion promoter composition according to Claim 1 to improve the adhesion of adhesive formulations to substrate surfaces, comprising the steps of:

5 mixing the adhesion promoter composition into an adhesive formulation or with the constituents of an adhesive formulation.

21. A method of using an adhesive formulation according to Claim 10 to bond together two substrates, comprising either:

- 5 (a) applying the adhesive formulation onto the surface of one of the substrates, and mating the second substrate thereover, or
- (b) applying the adhesive formulation into a space defined between two substrates having previously been brought toward one another.

22. A method of preparing an adhesive formulation according to Claim 10, comprising the step of:

mixing together

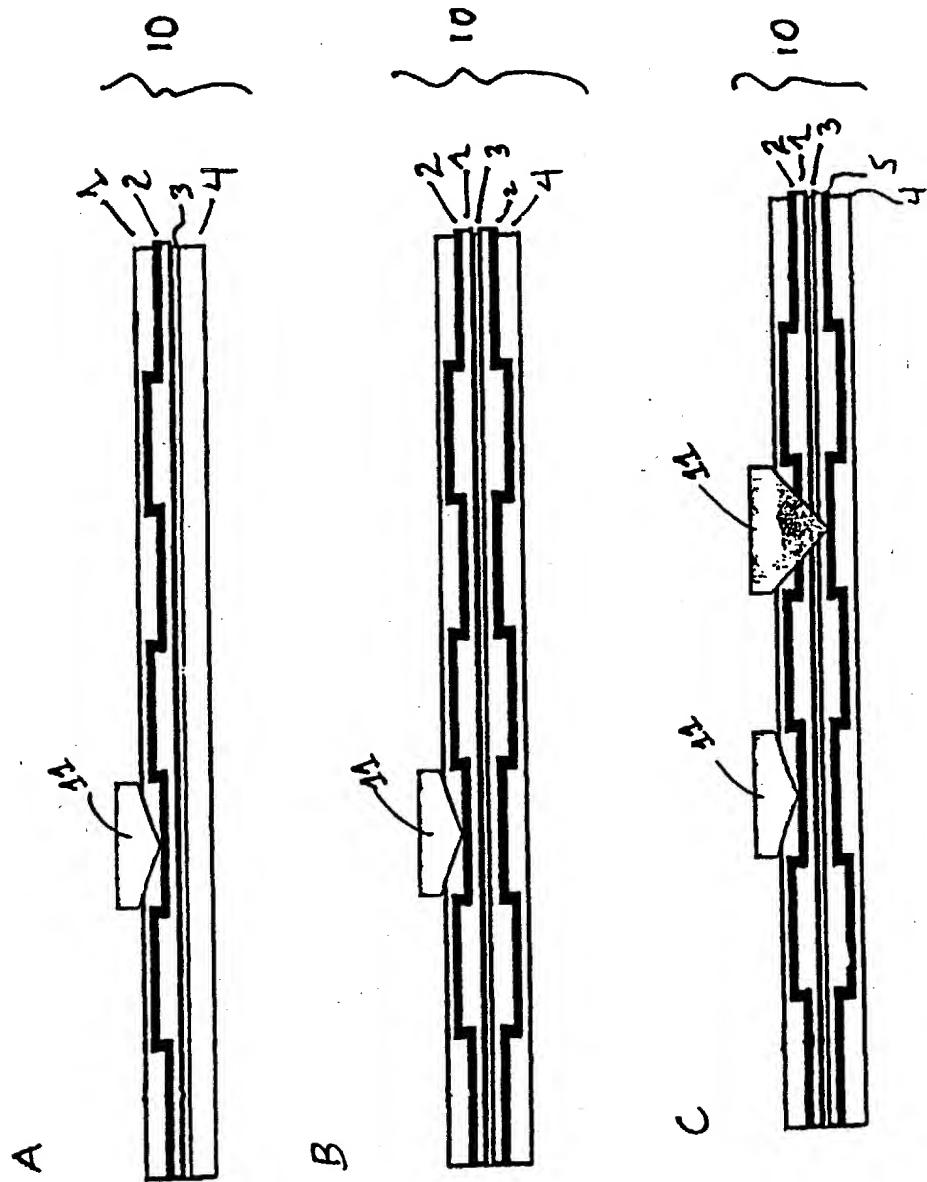
- 5 (a) a (meth)acrylate component; and
- (b) an adhesion promoter composition according to Claim 1.

23. An optical disk unit assembled with the adhesive formulation according to Claim 10, comprising:

- (a) a first substrate having a first facing surface,
- 5 (b) a second substrate having a second facing surface,

wherein said first and second facing surfaces face each other, and at least one of said first and second facing surfaces includes a recording layer, with a layer of the adhesive formulation according to Claim 10 disposed between said first and second facing surfaces of said first and second substrates.

FIG. 1



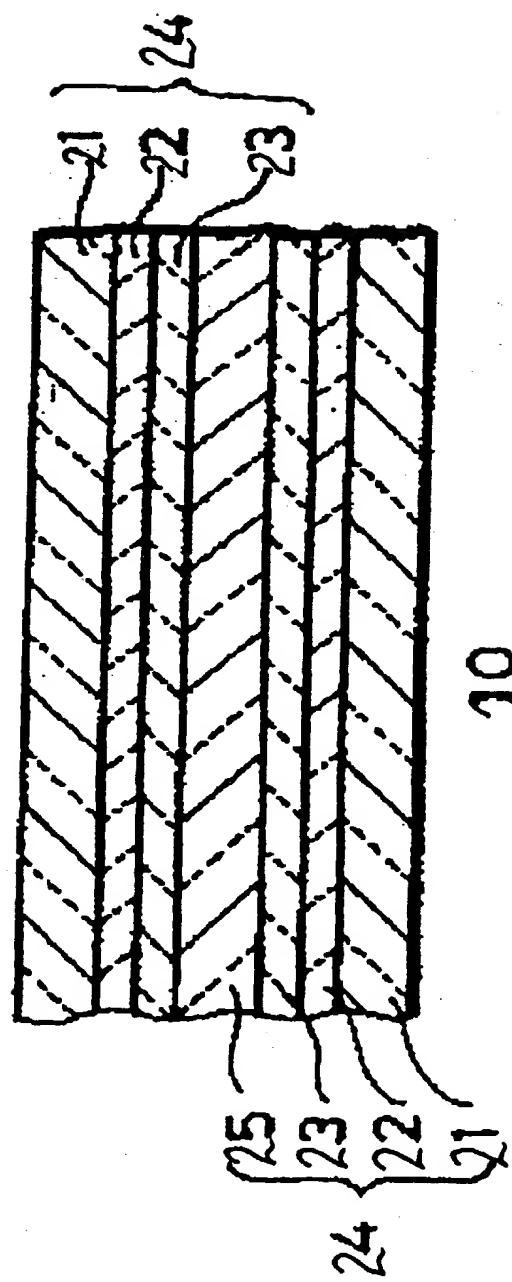


FIG. 2

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IE 00/00001

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C09J4/00 G11B7/24

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 C09J G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No.  |
|------------|---|------------------------|
| X          | EP 0 889 465 A (SUMITOMO CHEMICAL CO)<br>7 January 1999 (1999-01-07)<br><br>examples<br>claims  | 1,3,<br>9-19,<br>21-23 |
| X          | WO 98 45344 A (DSM NV ;SULLIVAN MICHAEL<br>GORDON (US); LAPIN STEPHEN (US); KRONGAUZ)<br>15 October 1998 (1998-10-15)<br>examples 4,21,22 | 1,3,<br>9-19,<br>21-23 |
| X          | US 5 320 933 A (LUNDY DANIEL E ET AL)<br>14 June 1994 (1994-06-14)<br>column 2, line 40 - line 45<br>examples                             | 1,6,9-22               |

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

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- "&" document member of the same patent family

Date of the actual completion of the International search

20 March 2000

Date of mailing of the International search report

30/03/2000

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## Authorized officer

Pollio, M

## INTERNATIONAL SEARCH REPORT

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| Int'l           | ional Application No |
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Character of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|--|-----------------------|
| X          | US 4 348 427 A (PRIOLA ALDO ET AL)<br>7 September 1982 (1982-09-07)<br>cited in the application<br>examples<br>claims                  | 1-3,9-15              |
| A          | US 5 698 285 A (KOJIMA KAZUHIRO)<br>16 December 1997 (1997-12-16)<br>cited in the application<br>column 3, line 28 - line 46<br>claims | 1-23                  |
| A          | US 5 663 211 A (KOMINAMI HIRAKU ET AL)<br>2 September 1997 (1997-09-02)<br>cited in the application<br>examples<br>claims              | 1-23                  |

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IE 00/00001

| Patent document cited in search report | Publication date | Patent family member(s) |  | Publication date |
|--|------------------|-------------------------|--|------------------|
| EP 0889465                             | A 07-01-1999     | CA 2242047 A            |  | 03-01-1999       |
|  |                  | CN 1208056 A            |  | 17-02-1999       |
|  |                  | JP 2891257 B            |  | 17-05-1999       |
|  |                  | JP 11073684 A           |  | 16-03-1999       |
|  |                  | US 5989778 A            |  | 23-11-1999       |
| WO 9845344                             | A 15-10-1998     | EP 0973815 A            |  | 26-01-2000       |
| US 5320933                             | A 14-06-1994     | NONE                    |  |                  |
| US 4348427                             | A 07-09-1982     | IT 1162770 B            |  | 01-04-1987       |
|  |                  | BE 884395 A             |  | 19-01-1981       |
|  |                  | DE 3027574 A            |  | 19-02-1981       |
|  |                  | DK 297480 A             |  | 11-02-1981       |
|  |                  | FR 2463168 A            |  | 20-02-1981       |
|  |                  | GB 2055860 A,B          |  | 11-03-1981       |
|  |                  | JP 56026918 A           |  | 16-03-1981       |
|  |                  | NL 8004190 A            |  | 12-02-1981       |
| US 5698285                             | A 16-12-1997     | JP 9169957 A            |  | 30-06-1997       |
| US 5663211                             | A 02-09-1997     | JP 7070472 A            |  | 14-03-1995       |